

# Luminescence of rare-earth ions and intrinsic defects in $\text{Gd}_2\text{O}_3$ matrix

**Yu A Kuznetsova, A F Zatsepin, R A Tselybeev, V N Rychkov, V A Pustovarov**  
Ural Federal University, Yekaterinburg, Russia

**Abstract.** The X-ray luminescence and photoluminescence of the ultradispersed  $\text{Gd}_2\text{O}_3$  powders with different purity were investigated in 90-360 K temperature range. Both impurity and intrinsic optical active centers were detected. The effect of energy transfer from  $\text{Gd}^{3+}$  to  $\text{RE}^{3+}$  ions was observed.

## 1. Introduction

Gadolinium oxide is of interest as a wide-band gap insulator ( $E_g = 5.6$  eV) for optoelectronics, photonics, fluorescence sensing, etc., because of its optical and chemical properties, in particular, the ability of being easily doped with rare-earth (RE) ions in a wide concentrations range. The trivalent RE ions doping such as Pr, Dy, Tb ions or Yb-Er, Yb-Ho, Yb-Tm pairs determines prospects of  $\text{Gd}_2\text{O}_3$  as down- and up-conversion material for energy transformation devices, including solar cells [1].

Energy and quantum efficiency of oxide matrixes doped with  $\text{RE}^{3+}$  is mainly determined by dynamic of excitation states of material electronic subsystem [2]. Processes of charge carrier transport, especially the probabilities of non-radiative relaxations, depend on crystal structure and defectiveness of the host lattice. In general, the low-symmetric modifications of host matrixes along with the intrinsic and impurity-related defects lead to the creation of additional luminescence quenching channels [2, 3]. On the other hand, there is information about enhancement the luminescence efficiency of RE-doped phosphors after co-doping that distorts the stoichiometry of lattice [4]. Thus, the investigation of matrix role in the spectral-optical properties of RE-doped materials will make it possible to find ways for improving of their functional characteristics.

In the present work we have studied the features of different excitation channels of RE luminescence in ultradispersed  $\text{Gd}_2\text{O}_3$  powders and revealed the influence of intrinsic defects on energy transfer processes.

## 2. Samples and Methods

The objects of this research were microstructured  $\text{Gd}_2\text{O}_3$  powders prepared by aqueous solution deposition method. The samples had different degree of purity and corresponded to the GdO-Zh (99.99 %) and GdO-G (99.9999 %) technical marks. The XRD profiles of these samples showed single cubic phase (Ia-3 space group) with lattice constants  $a = 10.81$  and  $10.79$  Å respectively. The average particle sizes of powders were estimated to be 8-10  $\mu\text{m}$  by means of FRITSH laser particle size analyzer.

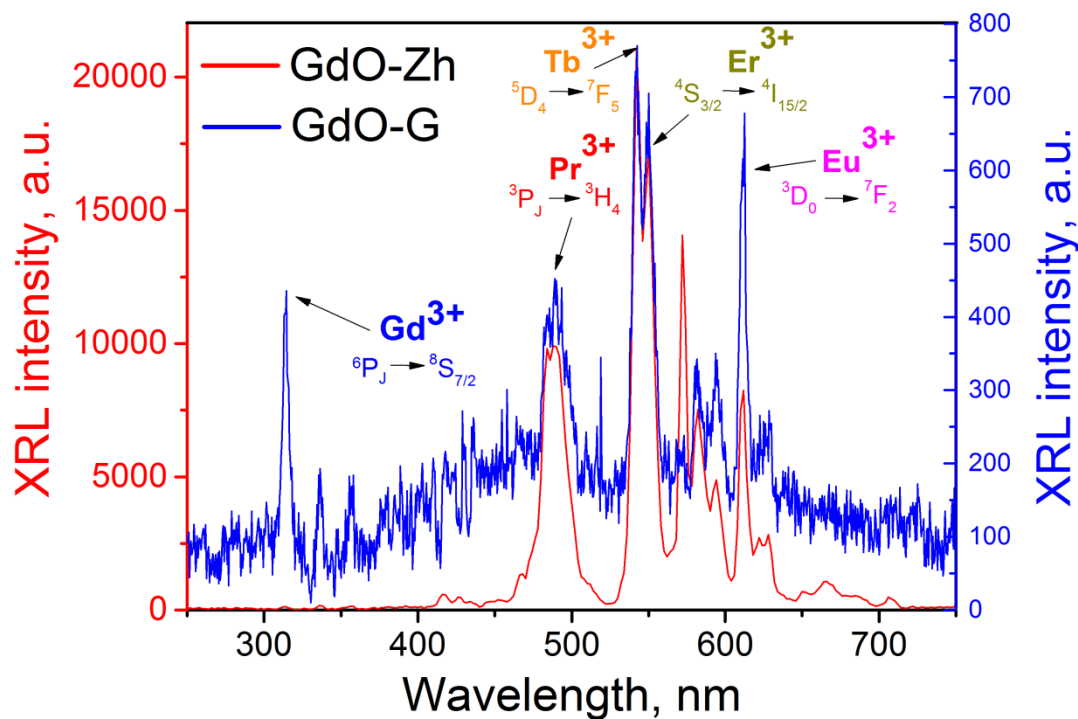
The X-ray excited luminescence (XRL) spectra were recorded by experimental setup equipped with BSV-2 X-ray tube with Mo anode at a voltage of 30 kV and current of 10 mA. The photoluminescence (PL) and PL excitation studies were performed on a setup assembled using 400 W deuterium lamp, R6358-10 Hamamatsu photomultiplier and two prismatic DMR-4 computer-controlled



monochromators. Low-temperature measurements were carried out by using vacuum cryostat ( $P = 10^{-4}$  Pa). The temperature of the sample was controlled by platinum resistance thermometer HRTS-5760-B-T-1-12 with accuracy of 1% and changed by the external heater inserted into a sample holder.

### 3. Results

In nominally pure  $\text{Gd}_2\text{O}_3$  powders under X-ray excitation at room temperature a number of narrow lines of luminescence in blue (489 nm), green (550 nm), yellow (572-594 nm) and red (612-628 nm) regions of the spectrum has been observed (figure 1). Based on the Dieke diagram these emission bands were attributed to the intraconfiguration  $f-f$  transitions of  $\text{Pr}^{3+}$ ,  $\text{Tb}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Eu}^{3+}$  ions existing in matrix as micro impurities. It should be noted that in the high-purity sample (GdO-G) quantum yield of impurity RE ions luminescence considerable decreases while  $^6\text{P}_J \rightarrow ^8\text{S}_{7/2}$  radiative transition of  $\text{Gd}^{3+}$  ions with 314 nm characteristic line is firstly detected.

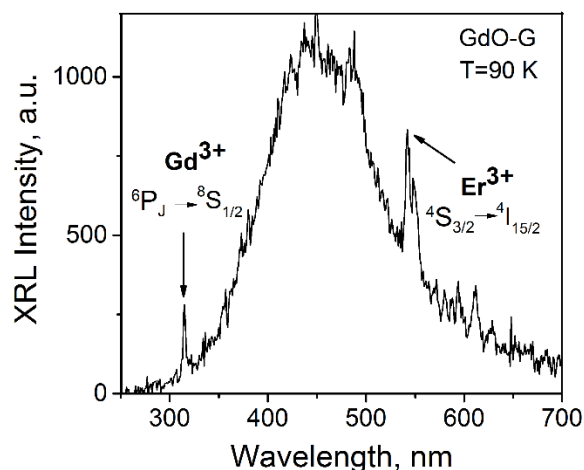


**Figure 1.** XRL spectra of GdO-Zh (99.99 % purity) and GdO-G (99.9999 % purity) samples at room temperature. Electron transitions corresponding to  $f-f$  emission of  $\text{RE}^{3+}$  impurity ions are shown by narrows.

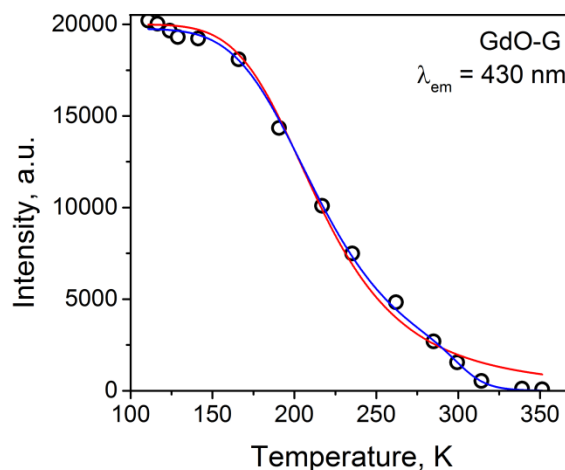
In low-temperature XRL spectrum of the GdO-G sample the narrow emission lines of  $\text{RE}^{3+}$  ions also appear but the most intense luminescence corresponds to the broad band centered at 430 nm with a full-width-half-maximum of about 130 nm (figure 2). The temperature dependence of the intensity of this band in the range 110-350 K is plotted in figure 3. The noticeable luminescence quenching starts at the 125 K approximately. At first, we tried to describe the obtained experimental data by the classic Mott's law that is valid for a single activation model. However, such approximation is satisfactory only at low temperatures up to 200 K (red line in figure 3). Therefore we have used the modified Mott's law expression that accounts for the realization of two-activated processes with different activation energies [5-7]:

$$I(T) = \frac{I_0}{1 + A_a \exp(-E_a/kT) + A_b \exp(-E_b/kT)} \quad (1)$$

$I_0$  is the intensity in the limit of low temperature;  $k$  is the Boltzmann constant;  $A_a$  and  $A_b$  are the pre-exponent factors reflected the non-radiative over radiative probability ratios;  $E_a$  and  $E_b$  are the activation energies, which characterize the height of the barriers of non-radiative relaxation channels. Using the equation 1 allows adequately describing the  $I(T)$  dependence over the whole investigated temperature range (blue line in figure 3). The parameters of fit are listed in table 1.



**Figure 2.** XRL spectra of GdO-G (99.9999 % purity) sample at 90 K temperature. The narrows represents the transitions of Gd<sup>3+</sup> host ions and Er<sup>3+</sup> impurity ions.

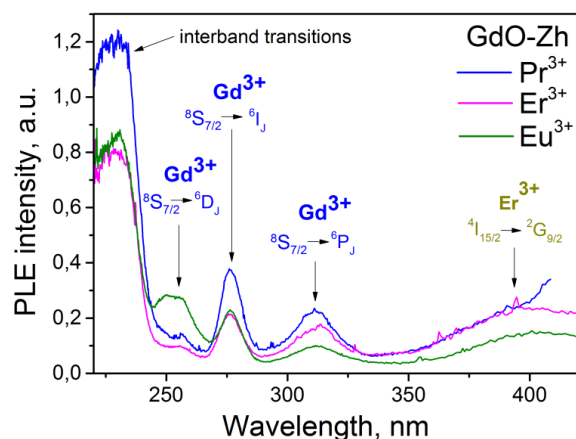


**Figure 3.** Temperature quenching of luminescence at 430 nm under X-ray excitation. The red line represents the approximation by classic Mott's law. The blue line corresponds to a double-activation Mott's law (equation (1)).

**Table 1.** Parameters of the quenching of luminescence at 430 nm for Gd<sub>2</sub>O<sub>3</sub> with 99.9999 % purity

$I_0$	$A_a$	$A_b$	$E_a$ (eV)	$E_b$ (eV)
$19760 \pm 113$	$1700 \pm 56$	$1.2E18 \pm 4E17$	$0.141 \pm 0.005$	$1.033 \pm 0.08$

The PL spectra recorded at room temperature under excitation corresponding to interband Gd<sub>2</sub>O<sub>3</sub> transitions (5.6 eV) demonstrated the lines at the same wavelengths as in XRL spectra (not shown here). The PL excitation spectra of Pr<sup>3+</sup>, Er<sup>3+</sup> and Eu<sup>3+</sup> ions are represented in figure 4. It was found that  $f \rightarrow f$  emission of RE<sup>3+</sup> can be efficiently excited by different ways: (i) – under intracenter excitation; (ii) – at energies corresponding to <sup>6</sup>P<sub>J</sub>, <sup>6</sup>I<sub>J</sub>, <sup>6</sup>D<sub>J</sub> excited states of Gd<sup>3+</sup> ions; (iii) – at energies more than 5.6 eV in the region of Gd<sub>2</sub>O<sub>3</sub> fundamental absorption edge [8].



**Figure 4.** PL excitation spectra of  $f \rightarrow f$  emission at 486 nm (Pr<sup>3+</sup>), 550 nm (Er<sup>3+</sup>) and 612 nm (Eu<sup>3+</sup>) for GdO-Zh (99.9999 % purity) sample at 295 K.

#### 4. Discussion

The obtained results clearly indicate that, firstly, there is efficient energy transfer by band charge carriers to impurity centers as evidenced by high X-ray luminescence output (figure 1). Secondly, the presence in excitation spectra the intense  $\text{Gd}^{3+}$  transition lines (figure 4) points out to non-radiative energy transfer from gadolinium to  $\text{Pr}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Eu}^{3+}$  ions.

The reduction of impurity ions concentration leads to decreasing of  $\text{Gd}^{3+} \rightarrow \text{RE}^{3+}$  energy transfer efficiency and simultaneous increasing the probability of radiative relaxation in  $\text{Gd}^{3+}$  ion (see figure 1). This fact is confirmed by the appearance of  ${}^6\text{P}_J \rightarrow {}^8\text{S}_{7/2}$  emission band in the XRL spectrum of greater purity sample (GdO-G) against the background of dramatically decreasing of luminescence intensity related to impurity  $\text{RE}^{3+}$  ions. It denotes that the radiative  ${}^6\text{P}_J \rightarrow {}^8\text{S}_{7/2}$  transition of  $\text{Gd}^{3+}$  and energy transfer to impurity  $\text{RE}^{3+}$  ions are competing processes.

The presence of local energy levels of  $\text{Gd}^{3+}$  ions in the region of  $\text{Gd}_2\text{O}_3$  optical transparency indicates the realization of the self-activation effect. In other words, matrix  $\text{Gd}^{3+}$  ions behave as extrinsic activators that act as energy donors. In different host lattices the nature of the self-activation centers has been related to the point distortions of lattice caused by deviations from stoichiometry [9, 10]. In our case, the most possible intrinsic defects involved in absorption and luminescence processes are either interstitial  $\text{Gd}^{3+}$  ions or  $\text{Gd}^{3+}$  at normal lattice sites associated with other nearest point defects. In any instances the local environment of the “defective”  $\text{Gd}^{3+}$  ions is distorted by internal crystal field. It results in partly weakening of the parity selection rule for  $f$ - $f$  transitions of  $\text{Gd}^{3+}$  as confirmed by the appearance of corresponding bands in XRL and PL excitation spectra [11].

Low-temperature band at 430 nm manifested in XRL spectra of the high-purity  $\text{Gd}_2\text{O}_3$  (figure 2), obviously, cannot be related to transition of any RE ions. The trivalent lanthanides are characterized by narrow emission lines originating from  $4f$  intraconfiguration transitions while the divalent rare-earth ions (for example,  $\text{Eu}^{2+}$ ) show broad  $5d$ - $4f$  luminescence but in another spectrum region [12, 13]. It is most likely that the nature of this band is associated with intrinsic defects of  $\text{Gd}_2\text{O}_3$  lattice acting as optically active centers. In cognate  $\text{La}_2\text{O}_3$  matrix the broad emission peak in the deep blue region has been attributed to single ionized oxygen vacancy [14]. Therefore we suggest that low-temperature luminescence at 430 nm also can be related with the presence of intrinsic lattice defects like  $F$ -centers.

The analysis of the temperature quenching curve of luminescence at 430 nm (figure 3) revealed that there are at least two non-radiative relaxation channels. The first activation process is realized at low temperatures (up to 200 K) and characterizes by  $E_a$  energy barrier value of 0.141 eV. The low activation energy along with a small value of probability  $A_a$  (table 1) indicates that the most likely this quenching process is intracenter. At the same time, at higher temperatures the another quenching channel with significantly higher barrier (1.033 eV) is dominant. For this case the non-radiative relaxation can also occurs within the center provided the complexity of configuration curves. However, it is possible that the second channel is due to the external quenching process with the transfer of excitation to other optically active centers. For detail information about luminescence quenching mechanisms the additional spectroscopic investigations are required.

#### 5. Conclusion

The luminescence of impurity  $\text{RE}^{3+}$  ions in  $\text{Gd}_2\text{O}_3$  powders has been detected. We have found that so called “defective”  $\text{Gd}^{3+}$  ions act as donors of excitation energy and presumably associated with intrinsic lattice defects. With decrease of impurity concentration the self-activated luminescence of  $\text{Gd}^{3+}$  has been observed. The low-temperature luminescence at 430 nm was assigned to the host lattice defects like  $F$ -centers. The analysis of temperature quenching revealed two non-radiative relaxation channels: in temperature region up to 200 K the intracenter quenching process is realized while at higher temperatures the second activation channel with a higher energy barrier prevails.

The obtained results indicate that the processes of energy transport and efficiency of radiative transitions in ultradispersed  $\text{Gd}_2\text{O}_3$  powders largely depend on intrinsic defects. The control of impurity composition and lattice disordering allows modifying the optical properties to improve the functional parameters of  $\text{Gd}_2\text{O}_3$ -based energy converters.

## Acknowledgments

This work was supported by the Ministry of Education and Science of Russia, the Grain-in-Aid Agreement no. 14.581.21.0002, September 29, 2014 (the unique identifier RFMEFI58114X0002) in the frame of the Federal Aim Program «Research and Development in Priority Directions of the Science and Technology Complex of Russia for 2014-2020». The part of results was obtained within the framework of the Act 211 Government of the Russian Federation (contract № 02.A03.21.0006).

## References

- [1] Strumpel C, McCann M, Beaucarne G et al 2007 *Sol. Energ. Mat. Sol. C.* **91** 238–249
- [2] Case M A, Bradford C Stout 2012 *Photoluminescence: Applications, types and efficacy* (New York: Nova Science Publishers, Inc.) p 55
- [3] Zhang J Z 2009 *Optical Properties and Spectroscopy of Nanomaterials* (Hackensack: World Scientific Publishing Co Pte. Ltd.) p 271
- [4] Liu B, Gu M, Liu X et al 2006 *J. Alloy. Compd.* **440** 341-345
- [5] Bieber H, Gilliot P, Gallart M et al 2007 *Catal. Today* **122** 101-108
- [6] Hirai T, Asahi M, Iwasaki Y et al 2009 *J. Lumin.* **129** 406-409
- [7] Zatsepin A F, Biryukov D Yu, Kortov V S, Cholakh S O 2002 *Phys. Solid State* **44** 1671–75
- [8] Dhananjaya N, Nagabhushana H, Nagabhushana B M et al 2012 *Spectrochim. Acta A* **96** 532-540
- [9] Chen Y N, Xu S J, Zheng C C et al 2014 *Appl. Phys. Lett.* **105** 041912
- [10] Wang T, Gou J, Xu X et al 2015 *Optics Express* **10** 12595-604
- [11] Kasap S, Capper P 2007 *Springer Handbook of Electronic and Photonic Materials* (New York: Springer Science-Business Media Inc.)
- [12] Biswas K, Sontakke A, Sen R, Annapurna K 2012 *J. Fluoresc.* **22** 745-752
- [13] Liu Z, Nengli D, Yang L, Li J 2015 *Appl. Phys. A* **119** 553-557
- [14] Hu C, Liu H, Dong W 2007 *Adv. Mater.* **19** 470-474